A STUDY OF THE

Nitrate and Sulphate of Orthodiazotoluene

AND THE

Action of the Sulphate on Methyl Alcohol.

DISSERTATION

SUBMITTED TO THE JOHNS HOPKINS UNIVERSITY FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

WILLIAM BROMWELL.

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ACKNOWLEDGMENT.

The following investigation was undertaken at the suggestion of Professor Remsen and was carried out under his personal supervision. I wish to express here my high appreciation of his constant encouragement and assistance, and to thank him for his uniform kindness since my first connection with this university. I would also express my obligation to Professor H. N. Morse, Professor W. B. Clark, and the late Professor G. H. Williams for instruction and advice.

Introduction.

The first work of Griess[1] on the diazo compounds led him, in 1866, to make the general statement that when they are decomposed by boiling alcohol, the diazo group is replaced by hydrogen, with the formation of the original hydrocarbon. Whereas, when the decomposition is effected by water a phenol is the result. The two reactions, in their simplest form, may be represented by the following expressions:

(1) $C_6H_5.N_2.NO_3 + CH_3OH = C_6H_6 + CH_2O + N_2 + HNO_3$

and

(2) $C_6H_5.N_2.NO_3 + HOH = C_6H_5OH + N_2 + HNO_3$.

But in 1870 Wroblewsky[2] found, on studying the decomposition of the isomeric chlortoluidines with alcohol, that, to some extent at least, the reaction was analogous to the case where water was used, the group C_2H_5O entering in place of the diazo group. This reaction, which is called the alkoxy reaction, in distinction from the so-called "hydrogen" reaction of Griess, is represented in its simplest form, thus:

$$C_6H_5.N_2.NO_3 + CH_3OH = C_6H_5.OCH_3 + N_2 + HNO_3.$$

Similar reactions have been observed by many writer, *viz.*: Hoffmeister,[3] Meyer and Stüber,[4] Hayduck[5], Ladenburg,[6] Fittaca,[7] Zander,[8] Balentine,[9] Payson,[10] Mohr,[11] Heffter,[12] Schulz,[13] Haller,[14] Hofmann,[15] Limprecht,[16] and others.

And, in 1882, Remsen and Broun,[17] first suggested that the position of the groups and the conditions under which the decomposition was accomplished might influence the course of the reaction.

1 Ann. chem. (Liebig), **137**, 68. 2 Ztsch. chem., **6**, 164; Ber. d chem. Ges., **3**, 98.
3 Ann. chem. (Liebig), **159**, 196. 4 Ann. chem. (Liebig). **165**, 187.
5 Ann. chem. (Liebig). **172**, 215. 6 Ber. d. chem. Ges., **8**, 1212.
7 Ber. d. chem. Ges., **11**, 1209. 8 Ann. chem. (Liebig), **198**, 25.
9 Ann. chem. (Liebig), **202**, 357. 10 Ann. chem. (Liebig), **221**, 215.
11 Ann. chem. (Liebig), **221**, 222. 12 Ann. chem. (Liebig), **221**, 351.
13 Ber. d. chem. Ges., **17**, 475. 14 Ber. d. chem. Ges., **17**, 1887.
15 Ber. d. chem. Ges., **17**, 1917. 16 Ber. d. chem. Ges., **18**, 2176, 2189.
17 Ann. chem. J., **4**, 374.

Since that time much work has been done in this laboratory on this subject under the immediate direction of Professor Remsen by Palmer,[1] Orndorff,[2] Graham,[3] Dashiell[4], Metcalf,[5] Parks,[6] Shober,[7] Beeson,[8] Weida,[9] and Cameron.[10]

During the last year Chamberlin[11] investigated the action of the nitrate and sulphate of paradiazotoluene on methyl alcohol under various conditions, and the work described in this paper is on the corresponding ortho compounds with a study of orthomethoxytoluene, the methyl ether of orthocresol.

Preparation of Orthotoluidine Nitrate.

Orthotoluidine nitrate is prepared as follows: 40 grams of nitric acid diluted with an equal volume of water are poured upon 40 grams of orthotoluidine and the mixture stirred in the cold. The nitrate crystallizes out and the mother-liquor is sucked off with a pump. After washing once with cold water, and draining as completely as possible, the white salt is dried upon a porous plate. The yield is almost theoretical; *viz.*, 62.5 grams.

Preparation of Orthodiazotoluene Nitrate.

The method of Knoevenagel[12] for the preparation of dry diazo salts was tried as follows:

Fifteen grams of orthotoluidine nitrate were dissolved in about 350 cc. of alcohol and the solution acidified with a few drops of nitric acid and cooled to 0°. 12.5 grams of amyl nitrite were now added slowly while stirring. After standing about fifteen minutes, ether was added to aid the separation of the diazo compound. This experiment was repeated several times, but in no case could the diazo nitrate be obtained in this way, except in very small quantities. It was apparently decomposed as fast as formed, even though the temperature was kept at 0°. The solution became very dark and there was an evolution of nitrogen. The best yield was obtained by passing nitrous fumes, derived from the action of nitric acid upon arsenic, through the orthotoluidine

[1] Am. chem. J., **8**, 243. [2] Am. chem. J., **9**, 387. [3] Am. chem. J., **11**, 319.
[4] Am. chem. J., **15**, 124. [5] Am. chem. J., **15**, 301. [6] Am. chem. J., **15**, 320.
[7] Am. chem. J., **15**, 379. [8] Am. chem. J., **16**, 244. [9] Dissertation, 1894.
[10] Dissertation, 1894. [11] Dissertation, 1894. [12] Ber. d. chem. Ges., **23**, 2994.

nitrate mixed to a thin paste with alcohol, and kept cold by a freezing mixture. After a time the salt went into solution, and finally a test with dilute caustic soda solution did not give the odor of toluidine. The action was then complete, and the solution was poured into strong alcohol (from lime), and ether slowly added with constant stirring till a permanent cloudiness resulted. As soon as the precipitation of the diazo compound commenced, more ether was added until no further precipitation was caused. The mixture was then allowed to stand for several hours, when the precipitate assumed a crystalline character, and was much more easily washed than when freshly precipitated, when it is usually somewhat gummy. It was then drained as completely as possible from the mother-liquor with the aid of the pump, and washed several times with cold absolute alcohol, and then with ether until the washings were colorless. The ether was then sucked off as completely as possible, and the crystals spread upon a porous plate to dry. When first washed with ether they were very light brown, but rapidly darken upon exposure on the plate.

The first time the nitrate was prepared for this investigation it remained on the plate for about twenty-four hours, when it had become very dark and moist Upon close examination it was found to be studded with minute fine yellow needles and smelled strongly of cresol. While preparing to pick out some of these needles to determine their melting-point, the whole mass (about 38 grams) was decomposed with violent explosion. The only apparent cause for the explosion was the heat from a Bunsen burner, which was burning at a distance of about twenty inches from the plate. The temperature could not have been raised more than a very few degrees.

A second lot of the nitrate (approximately 40 grams) was prepared in exactly the same way, and to avoid the possibility of an explosion care was taken to see that no flame was within 10 feet of it. However, upon taking it from the funnel and spreading it upon the porous plate to remove the last traces of ether, it immediately exploded with terrific violence, without any apparent cause. The force of the explosion was

so great that the plate was broken in small pieces, and the top of the table was badly shattered. All the gas burning in the room was extinguished, and the noise was so great that some of the men working in the room were temporarily deafened. The author's hand was injured to such an extent that it could not be used for nearly six weeks. As the nitrate was so unstable, upon resumption of work, the investigation was confined for the present to the sulphate.

PREPARATION OF ORTHODIAZOTOLUENE SULPHATE.

The preparation of orthodiazotoluene sulphate is much more easily accomplished than that of the corresponding nitrate. The Knoevenagel method, that involving the use of amyl nitrite, was tried, and found to be very satisfactory, but the results were not materially better than those obtained by the use of the nitrous fumes from arsenic and nitric acid. The former is slightly quicker, but the presence of the amyl alcohol makes the recovery of the ordinary alcohol and ether more difficult. Therefore the following method, that used by Remsen and Orndorff[1] for this compound, and by Chamberlin[2] for the corresponding para compound was adopted.

25 grams of pure orthotoluidine are dissolved in 250 cc. of ordinary alcohol in an Erlenmeyer flask, and a slight excess (25 grams) of sulphuric acid carefully added, drop by drop, with constant shaking until the orthotoluidine sulphate thus formed has dissolved. The flask is now placed in ice water and the fumes from nitric acid and arsenic, after passing through two wash bottles immersed in ice water to cool the gases and to condense any nitric acid, are conducted into the solution until the reaction is complete, usually requiring from one to two hours. This is best told by the appearance of the crystailine precipitate. The crystals of the orthodiazotoluene sulphate are fine well-characterized needles, which are heavier than the irregular flaky crystals of orthotoluidine sulphate. The action of the nitrous fumes is then stopped, and the crystals filtered off, and to the filtrate ether is added when, after standing in an ice-bath for several hours, a second crop of crystals is obtained. The crystals are first washed with ordinary alcohol, and then with absolute alcohol till the washings

[1] Am. Chem. J., 9, 394. [2] Dissertation, 1894.

are colorless. The alcohol is then washed out with anhydrous ether, which is sucked off as completely as possible with the pump. The salt is then spread out on a porous plate and the last trace of ether rapidly disappears. Sometimes the salt has a bluish-green color, and at others it is nearly white, turning pink on washing with alcohol. Exposed to the air on the porous plate at ordinary temperatures, the salt is comparatively stable, no signs of explosion having been noticed, and only slight changes in color taking place in twenty-four hours.

The *methyl alcohol* used in these experiments was that sold as "Columbian Spirit," and obtained from H. C. Collier, Binghampton, N. Y. It was carefully compared with the best German methyl alcohol, and was found to compare very favorably with it, having slightly less of the empyreumatic odor. The German article contained slightly less water than the "Columbian Spirit," but the following experiments show that there is very little difference between them.

250 cc. each of the two kinds of methyl alcohol were treated with lime for eighteen hours and then distilled.

The German sample began to distil at 64°, and the temperature immediately rose to 65.2°, and stayed at about 65° until all but the last few drops had come over. The "Columbian Spirit" started at 64° and rose steadily to 66°.

Now 50 cc. each of these distillates were redistilled. The German sample in this case distilled between 64.5° and 65°, while the "Columbian Spirit" ranged from 64° to 66°, and just as the last few drops went off the temperature rose to 68°.

These experiments indicate that there was a little more water in the American specimen. Therefore the prolonged action of lime was tried, and it was found that, after standing for forty-eight hours, nearly all of a 750 cc. sample boiled exactly at 65° with a Hempel distilling tube.

As this is perfectly satisfactory, the alcohol used in the following experiments was all prepared in this way from the "Columbian Spirit," the cost of which is just about one-fourth that of the imported article.

Action of Methyl Alcohol on Orthodiazotoluene Sulphate.

1. *At the Ordinary Room Temperature.*—About 30 grams of

dry orthodiazotoluene sulphate were placed in a long-necked balloon-flask of about two liters capacity, and treated with 100 cc. of methyl alcohol (from lime). The flask provided with a return condenser was allowed to remain at the room temperature, about 20°. The action commenced at once, and there was quite a brisk evolution of nitrogen, but no perceptible odor of aldehyde. If the flask is left undisturbed the action is completed in about twenty hours, but it may be materially hastened by frequent shaking. It was then boiled on the water-bath for a short time to insure complete decomposition.

350 grams of orthodiazotoluene sulphate in portions of 30–40 grams were decomposed in this way with about 1400 cc. of methyl alcohol. The various portions were united and the alcohol distilled off on the water-bath. This distillate was added to about five times its volume of a saturated solution of common salt, when an oil of a pale yellow color slowly separated and rose to the surface. Water was then added to the residue remaining in the flask, and the distillation continued with steam. A yellow oil distilled over with the water. Its specific gravity is very nearly that of water. The residue in the flask consisted of a clear liquid and a black tarry substance, which later became quite hard and brittle upon cooling. The temperature was reduced to 0°, and the liquid filtered off and evaporated. Nothing except sulphuric acid was found in the residue. The tar, a black solid mass, was extracted with alcohol and most of it went into solution, but nothing was obtained from it.

The oils were then washed and dried over calcium chloride. They both have the same pleasant aromatic odor, suggesting that of the oil of wintergreen, but still quite different from it.

35 grams of the oil were obtained in this way from the alcoholic distillate. Upon distilling this only a few drops came over as the thermometer went steadily up to 160°, nearly all coming over between 164° and 174°, only about 1 gram being left in the flask at 174°.

97 grams of the oil were obtained from the steam distillate; 73 grams came over between 164° and 170°; and most of the rest between 170° and 174° leaving as above, only about 1 gram

in the flask. These two portions of oil, boiling between 164° and 174°, being apparently identical, were united and set aside.

2. *At a temperature near that of the boiling point of the alcohol.*— 400 grams of orthodiazotoluene sulphate were decomposed by heating the flask, provided with a return condenser and containing about 30 grams of the salt and about 100 cc. of absolute methyl alcohol, on the water-bath at about 50°–60° for about half an hour, when the action was apparently complete. The contents of the flask were then boiled for a few minutes to insure complete decomposition. The various portions decomposed in this way were united, and were then treated exactly as in the preceding experiment. The alcohol was distilled off, and 46 grams of oil were obtained from the alcoholic distillate on treatment with the strong solution of common salt.

The distillation was then continued with steam and 115 grams of the oil were thus obtained.

The oil obtained from the alcoholic distillate was washed, dried, and distilled, nearly all of it coming over between 164° and 174°.

The oil from the steam distillate was then treated in the same way, and nearly all of it came over between the same points, only about 5 grams coming over below 160°, and about 12 grams above 174° from both the portions.

The oil from all the various portions was then brought together and fractionated, and it was found that of the 293 grams of oil obtained altogether, 247 grams (over 84 per cent.) distilled between 167° and 170°. The average boiling point of this portion 168.5, corrected for the column of mercury outside of the vapor of the oil is 171.35°.

The boiling-point of the methyl ether of orthocresol, $C_6H_4\begin{smallmatrix}CH_3\\OCH_3\end{smallmatrix}$, as given by Pinnette[1] is 171.3°. Thus it will be seen that the principal action of methyl alcohol on orthodiazotoluene sulphate may be expressed by the following equation:

$$C_6H_4\begin{smallmatrix}CH_3\\N=N.HSO_4\end{smallmatrix} + CH_3OH = C_6H_4\begin{smallmatrix}CH_3\\OCH_3\end{smallmatrix} + H_2SO_4 + N_2.$$

[1] Ann. Chem. (Liebig), **243**, 37.

This corresponds to the decomposition of the same diazo salt with ordinary alcohol, as observed by Remsen and Orndorff,[1] who obtained as the chief product, the ethyl ether of orthocresol. If toluene was formed it was in such small quantities as to escape their notice. In these experiments, however, when larger quantities were used, there was enough of the oil boiling below 130° to enable us to prove the presence of toluene. This was done by adding a few drops of the oil to hot fuming nitric acid and pouring the mixture into water. On standing, crystals separated out which melt at 55°, and are, therefore, paranitrotoluene. No odor of formic aldehyde was observed during any of the decompositions. Apparently there was slightly more of the low-boiling oil formed in the second experiment where the decomposition was effected at the higher temperature, though the difference was so slight, and the quantities of toluene so small in both cases that no conclusion of value can be drawn.

Orthomethoxytoluene, or the Methyl Ether of Orthocresol.

The methyl ether of orthocresol was made by Pinnette[2] from phenol, potassium hydroxide, and methyl iodide, according to the Williamson reaction, and is described by him only as boiling at 171.3° and as having the specific gravity 0.9957 at 0°. In consideration of the fact that this is the only knowledge we have of the substance it was thought well to study it a little further. It is a colorless, very highly refracting, mobile oil with a rather pleasant aromatic odor, as above described as suggesting the oil of wintergreen, though differing markedly from it. It is almost insoluble in water, but easily soluble in alcohol and ether.

Action of Sulphuric Acid on Orthomethoxytoluene.

Forty grams of orthomethoxytoluene were poured slowly into 120 grams of concentrated sulphuric acid. Action took place at once, the oil going into solution with the formation of a decided rose color. The mixture was shaken for a few minutes to insure complete reaction, and it was then poured

[1] Am. Chem. J. 9, 387. [2] Ann. chem. (Liebig,) 243,37.

into about a liter and a half of water contained in a large evaporating dish, and was neutralized with barium carbonate, heat being applied to expel the carbon dioxide. The barium sulphate and the excess of barium carbonate were filtered off and the filtrate evaporated to crystallization. On cooling, the mother-liquor was sucked off from the crystals of the barium salt of orthomethoxytoluenesulphonic acid. This salt was recrystallized and the appearance of the crystals, which were small, transparent, glistening plates, and also still smaller white granules, suggested the possibility of two sulphonic acids.

Therefore, the salt was subjected to careful and prolonged fractional crystallization. Specimens of the salts from the extremes and from the middle of the series of fractions were taken and from these were made first the sodium salts. These were treated with phosphorus pentachloride and the sulphone chlorides obtained. These were solid and were apparently all the same. They were now treated with ammonia and the amides were thus made and recrystallized. All three amides melt sharply at 137°, and are therefore derived from the same sulphonic acid. This in turn shows that the result of treating the methyl ether of orthocresol is beyond doubt only one sulphonic acid. As this acid has not been described in the literature, it was decided to make and study some of its salts and derivatives.

Hayduck[1] decomposed orthodiazoparatoluene

sulphonic acid with methyl alcohol and obtained orthomethoxyparatoluene sulphonic acid, the barium salt of which he describes as crystallizing in small shining plates with two molecules of water of crystallization, which it does not lose over sulphuric acid.

The barium salt to be presently described as made from orthomethoxytoluene by treatment with sulphuric acid and

[1] Ann. chem. (Liebig), **172**, 217.

neutralizing with barium carbonate, agrees closely with that made by Hayduck. The latter, as above mentioned, crystallized with whitish irregular crystals mixed with shining transparent plates. In the course of fractional crystallization it is observed that it depends largely on the concentration of the solution which kind of crystals predominates. If the solution is comparatively weak the crystals are nearly all shining plates; but if the solution is quite concentrated the white opaque crystals are the rule. In a sample of the shining plates the water of crystallization was determined and found to correspond closely to the formula

$$\left(C_6H_3\begin{cases}CH_3\\OCH_3\\SO_3\end{cases}\right)_2 Ba.2H_2O.$$

Calculated 6.26. Found 6.18.

In another sample of the opaque variety the water and barium were estimated with the following results:

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\OCH_3\\SO_3\end{cases}\right)_2 Ba.H_2O.$	Found.
H_2O	3.23	3.83
Ba	24.43	24.37

It is thus seen that the salt crystallizes sometimes with one and sometimes with two molecules of water of crystallization. It is also almost impossible to obtain a crop of crystals entirely of either form. For this reason the analyses do not give especially good results.

Remsen and Parks[1] noted a similar influence of the concentration of the solution on the crystallization of the barium salt of paramethoxyorthotoluene sulphonic acid.

Orthomethoxytoluene Sulphonic Acid.

As it seemed desirable to make a further study of this acid and its salts, some of the free acid was prepared by exactly neutralizing a solution of the barium salt with dilute sulphuric acid. The barium sulphate was filtered off, and the filtrate evaporated down to a small bulk. The acid is very soluble

[1] Am. chem. J., 15, 320.

in water and in order to make it crystallize a few drops of a saturated solution of common salt were added as recommended by Gattermann,[1] whereupon crystallization immediately commenced with the formation of beautiful stellate clusters of short needles throughout the whole solution. The acid is filtered off, and when dried found to melt at 212°.

SALTS OF ORTHOMETHOXYTOLUENE SULPHONIC ACID.

Calcium Salt, $\left(C_6H_3\begin{cases}CH_3\\OC_2H_3\\SO_3\end{cases}\right)_2 Ca.9H_2O$.—This salt was prepared by neutralizing a solution of the free acid with finely pulverized calcite. It is very soluble in water and slightly less so in alcohol. From water it crystallizes in large, colorless, transparent plates, which are very efflorescent. Analysis for water and calcium gave the following results:

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\OCH_3\\SO_3\end{cases}\right)_2 Ca.9H_2O$.	Found. I.	Found. II.
H_2O	26.82	26.82	26.51
Ca	6.62	6.60	6.68

Magnesium Salt, $\left(C_6H_3\begin{cases}CH_3\\OCH_3\\SO_3\end{cases}\right)_2 Mg.5\frac{1}{2}H_2O$. — This salt was prepared either by neutralizing the free acid with pure magnesium carbonate or oxide, or by *exactly* precipitating the barium from a solution of the barium salt by means of a dilute solution of pure magnesium sulphate. The salt is easily soluble in water, but crystallizes well from it in large, well-developed, colorless, transparent prisms, which are unchanged by exposure to the air. Analysis for water and magnesium gave the following results:

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\OCH_3\\SO_3\end{cases}\right)_2 Mg.5\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	18.85	19.11	19.03
Mg	4.57	4.56	4.42

Zinc Salt, $\left(C_6H_3\begin{cases}CH_3\\OCH_3\\SO_3\end{cases}\right)_2 Zn.6\frac{1}{2}H_2O$.—This salt may be pre-

[1] Ber. d. chem. Ges., **24**, 2121.

pared in the same ways as the magnesium salt. It was found most convenient to make it by neutralizing the solution of the free acid with very finely powdered magnesium oxide. It crystallizes from water, in which it is easily soluble, in large, colorless, transparent rectangular plates, which lose part of their water on exposure to the air. Analysis for water and zinc gave the following results:

	Calculated for $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{smallmatrix}\right)_2 Zn.6\frac{1}{2}H_2O$	Found. I.	Found. II.
H_2O	20.03	19.42	19.84
Zn	11.13	10.70	10.98

Copper Salt, $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{smallmatrix}\right)_2 Cu.\ 6H_2O$.—The preparation of this salt was accomplished by exactly neutralizing a solution of barium salt with a solution of copper sulphate. The crystals are small, transparent, apple-green prisms, many of which have an apparently hexagonal section. They are easily soluble in water and are quite stable in the air. Analysis for water and copper gave the following:

	Calculated for $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{smallmatrix}\right)_2 Cu.\ 6H_2O.$	Found. I.	Found. II.
H_2O	18.85	18.62	18.52
Cu	10.99	10.74	10.64

Lead Salt, $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{smallmatrix}\right)_2 Pb.\ 6H_2O$.—This salt was made by treating a solution of the free acid with lead carbonate, heating, and filtering off the excess of carbonate. It crystallizes from its water-solution in thin leaflets with a pearly luster. These lose water, and with it their luster, on exposure to the air. This salt is quite unstable, decomposing within a few degrees of the point at which it ceases to give off water of crystallization, *i. e.*, approximately at 115°.

Much difficulty was experienced in the analysis of this salt both for the water, on account of the above-mentioned fact, and also in the case of the lead, because of the ease with which lead sulphate is reduced. The analysis was most sat-

isfactorily made in the following manner: The salt is weighed into a porcelain crucible and heated in the air-bath to about 110° to constant weight. It is now treated with a drop of sulphuric acid and one or two drops of nitric acid and heated carefully. When dry, more nitric acid is added as needed to oxidize the carbon. When this is accomplished a few drops of aqua regia are added and the crucible *very* gently heated for some time. Then sulphuric acid is added and evaporated repeatedly at as low a temperature as possible. It is finally brought to a dull red heat, until the free sulphuric acid has all been driven off. It is then cooled and weighed. The results came low in every case, and only by working with the utmost care as above described could approximate results be obtained.

	Calculated for $\left(C_6H_3(CH_3)(OCH_3)(SO_3)\right)_2Pb, 6H_2O$.	Found.
H_2O	15.06	15.50
Pb	28.77	28.54

Sodium Salt, $C_6H_3(CH_3)(OCH_3)(SO_3Na) \cdot 5\frac{1}{2}H_2O$.—This salt was made by *exactly* neutralizing a solution of the barium salt with a solution of sodium sulphate. It crystallizes in large, colorless, transparent needles which rapidly lose water on exposure to the air. Analysis for water and sodium gives the following results:

	Calculated for $C_6H_3(CH_3)(OCH_3)(SO_3Na) \cdot 5\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	30.65	29.53	29.22
Na	10.27	10.21	10.89

Potassium Salt, $C_6H_3(CH_3)(OCH_3)(SO_3K), \frac{1}{2}H_2O$.—This was prepared exactly as the sodium salt. It is so very easily soluble in water that it was found to be impossible to obtain it well crystallized from that solvent. It is much less easily soluble in alcohol, and from this it is obtained under certain conditions, in small, transparent, rhombic plates. Analysis for water and potassium gave the following results:

	Calculated for $C_6H_3(CH_3)(OCH_3).SO_3K.\frac{1}{2}H_2O$.	Found.
H_2O	3.61	3.91
K	16.25	16.31

Orthomethoxytoluenesulphone Chloride, $C_6H_3(CH_3)(OCH_3).SO_2Cl$.—The sodium salt prepared as above described was thoroughly dried in the air-bath at 120° and powdered. After cooling, it was treated with a slight excess of phosphorus pentachloride. Action was brought about by rubbing the two together in a dry evaporating dish with a dry pestle. Action took place quite readily, and after it was over and the mixture had cooled, cold water was added, upon which the chloride, which was at first soft, became quite hard and brittle, so that it was easily powdered and washed. A part of this was now dissolved in ether, from which it solidifies in a compact white crystalline mass. The reaction between the sodium salt and phosphorus pentachloride is represented by the following equation:

$$C_6H_3(CH_3)(OCH_3).SO_2ONa + PCl_5 = C_6H_3(CH_3)(OCH_3).SO_2Cl + POCl_3 + NaCl.$$

An estimation of chlorine gave the following results:

	Calculated for $C_6H_3(CH_3)(OCH_3).SO_2Cl$.	Found.
Cl	16.78	16.34

Orthomethoxytoluenesulphone Amide, $C_6H_3(CH_3)(OCH_3).SO_2NH_2$.—This was made by treating the sulphone chloride, which has just been described, with ammonia, and allowing the mixture to stand for several hours. Most of the ammonia was now evaporated off, as the sulphone amide was found to be somewhat soluble in it. On cooling, the crystals were separated from the mother-liquor, and recrystallized from hot water.

As thus obtained, they are beautiful, fine, white needles, which melt at 137°. Analyses gave the following results:

	Calculated for $C_6H_3(CH_3)(OCH_3).SO_2NH_2$.	Found.		
		I.	II.	III.
N	6.98	7.13	7.18	7.04
C	47.73	47.69	....	....
H	5.64	5.43	....	....

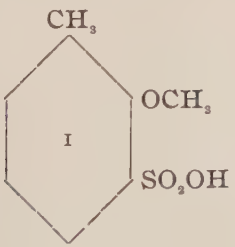
The figures under I. for nitrogen, carbon, and hydrogen, were kindly furnished by Mr. C. D. Ragland. The nitrogen in this, as in the second case by Messrs. J. W. Lawson and E. S. Smith, was estimated by the Dumas method. The third estimation of nitrogen, furnished by Mr. Lawson, was made by the Kjeldahl method.

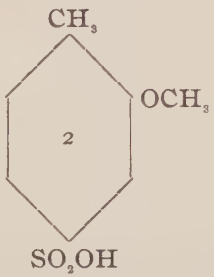
Further Discussion of Orthomethoxytoluene Sulphonic Acid.

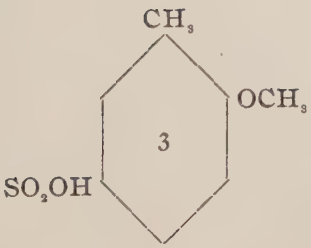
From a study of the preceding compound, it is seen that, when orthomethoxytoluene is treated with sulphuric acid only one acid residue enters into the compound; *i. e.*, that the reaction is expressed by the following equation:

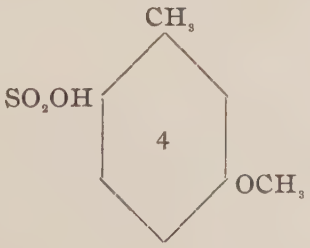
$$C_6H_4\begin{cases}CH_3\\OCH_3\end{cases} + H_2SO_4 = C_6H_3\begin{cases}CH_3\\OCH_3\\SO_2OH\end{cases} + H_2O.$$

Now, of course, we know that the methyl group and the methoxy group are in the ortho position to each other, but we have no knowledge whatever of the position of the sulphonic acid group. There are evidently the four possibilities expressed in the following formulas:









In studying the influence of different substituting groups in the benzene ring upon the position to be taken by a second substituting group, Professor Remsen[1] shows that the rule is that while acid groups cause substitution mainly in the meta position, neutral and basic groups cause substitution mainly in the para position, and, to some extent, in the ortho position. For example, if we treat toluene, aniline, phenol, etc., with sulphuric acid the principal product is the para compound, while the carboxyl and the nitro groups force the sulphonic acid group to the meta position. In view of these facts we should rather expect to find the sulphonic acid group in the position indicated in formula 2, were it not for the presence of the methoxy group, whose influence we should expect to find directing it toward the position indicated by the third formula. It was thought that it would be easy to pass from the sulphone amide, $C_6H_3\begin{cases}CH_3\\OCH_3\\SO_2NH_2\end{cases}$, made as has already been described, to orthomethoxysulphamine benzoic acid, $C_6H_3\begin{cases}COOH\\OCH_3\\SO_2NH_2\end{cases}$, by oxidation with potassium permanganate; and from this, by fusion with potassium hydroxide, to one of the three possible dihydroxybenzoic acids, $C_6H_3\begin{cases}COOH\ (1)\\OH\ (2)\\OH\ (x)\end{cases}$ which are known. To accomplish this the following experiments were performed:

Formation of Orthomethoxysulphamine Benzoic Acid.—Ten grams of the sulphone amide, as formed above, were treated with 34 grams of potassium permanganate in about a liter of water. These were heated in a balloon-flask with a return condenser from eight to ten hours, when the permanganate was completely reduced. In case this should not be so, a few drops of alcohol may be added to complete the reduction. The oxides of manganese were now filtered off, and the solution containing the potassium salt of the acid was evaporated to a small volume. It was then acidified with hydro-

[1] Theoretical Chemistry, 4th ed., p. 313.

chloric acid, when the free acid, $C_6H_3\begin{cases}\diagup COOH\\ OCH_3\\ \diagdown SO_2NH_2\end{cases}$, crystallized out. This was filtered off and dissolved in a dilute solution of sodium carbonate to separate it from any amide which may have been unoxidized. It was filtered, reprecipitated with hydrochloric acid, again filtered, recrystallized, and analyzed for sulphur and nitrogen with the following results:

	Calculated.	Found.
S	13.81	13.85
N	6.06	6.67

The melting-point is 211°.

The change here described is represented thus:

$$C_6H_3\begin{cases}\diagup CH_3\\ OCH_3\\ \diagdown SO_2NH_2\end{cases} + 3O = C_6H_3\begin{cases}\diagup COOH\\ OCH_3\\ \diagdown SO_2NH_2\end{cases} + H_2O.$$

Formation of Dihydroxybenzoic Acid.—To about 10–12 grams of potassium hydroxide, in a silver crucible, a few drops of water were added. Heat was then gently applied, and the mass melted. While still fused, 3 grams of the orthomethoxysulphamine benzoic acid were added gradually. Care was taken to keep the temperature as little above the melting-point of the mixture as possible during the reaction, in order to avoid breaking up the carboxyl group with the elimination of carbon dioxide. The mixture was heated until a few drops of it, dissolved in a little water, gave off sulphur dioxide upon treatment with hydrochloric acid, showing the formation of potassium sulphite. The mass was then allowed to cool, dissolved in water, and acidified. It was then evaporated to crystallization, cooled, filtered, and recrystallized, appearing either as moderately large needles or as very small, short prisms. The changes which we suppose to have taken place here may be represented thus:

$$C_6H_3\begin{cases}\diagup COOH\\ OCH_3\\ \diagdown SO_2NH_2\end{cases} + 5KOH =$$

$$C_5H_3\begin{cases}\diagup COOK\\ OK\\ \diagdown OK\end{cases} + NH_3 + K_2SO_3 + CH_3OH + H_2O;$$

$$C_6H_3\begin{matrix}\diagup COOK\\ \\ \diagdown OK\end{matrix}\!\!-OK + 3HCl = C_6H_3\begin{matrix}\diagup COOH\\ \\ \diagdown OH\end{matrix}\!\!-OH + 3KCl.$$

The substance thus obtained was well crystallized and melts fairly well at about 230° with evolution of a gas. A drop of a solution of ferric chloride added to a very dilute aqueous solution of the compound gives a deep red color. It does not reduce Fehling's solution.

Now upon studying the four known dihydroxybenzoic acids, with one of which it might be possible for this to be identical, we find that their characteristic properties are as here given.

The 1, 2, 3 acid,[1] $C_6H_3\begin{matrix}\diagup COOH\ (1)\\ \\ \diagdown OH\ (3)\end{matrix}\!\!-OH\ (2)$, melts at 204° and is colored dark blue by a solution of ferric chloride. It crystallizes in "water-free warts" or in needles with two molecules of water.

β-resorcylic acid, the unsymmetric metadihydroxybenzoic acid,[2] $C_6H_3\begin{matrix}\diagup COOH\ (1)\\ \\ \diagdown OH\ (4)\end{matrix}\!\!-OH\ (2)$. Its melting-point when free from water, is variously stated as 194°, 197°, 194°–200°, 204°–206°, and 213°. It is described as crystallizing with $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, and 3 molecules of water, according to circumstances. It does not reduce Fehling's solution. When heated above its melting-point it loses carbon dioxide and is converted into resorcin.

Oxysalicylic acid, $C_6H_3\begin{matrix}\diagup COOH\ (1)\\ \\ \diagdown OH\ (5)\end{matrix}\!\!-OH\ (2)$, melts, according to various authorities, at 196°–197°, or 199°–200°. Ferric chloride colors its solution deep blue. It reduces Fehling's solution.

The acid $C_6H_3\begin{matrix}\diagup COOH\ (1)\\ \\ \diagdown OH\ (6)\end{matrix}\!\!-OH\ (2)$ is described by Senhofer and Brunner.[3] It melts from 148°–167°. Its solution is colored

[1] Ann. chem. (Liebig), **220**, 116.
[2] Ann. chem. (Liebig), **161**, 11; Am. chem. J., **2**, 169; Ber. d. chem. Ges., **18**, 1985.
[3] Wiener Akademieber. (1879), 80.

violet by ferric chloride, and it reduces Fehling's solution.

All of these acids give off carbon dioxide, forming the corresponding dihydroxy derivative of benzene.

We observe now that the compound obtained by fusing orthomethoxysulphamine benzoic acid with potassium hydroxide does not correspond exactly to any of these acids. It agrees with β-resorcylic acid (1, 2, 4) in being colored red by ferric chloride, and in not reducing Fehling's solution. But its melting-point is too high, and it does not form fluoresceïn when heated with phthalic anhydride. It is suspected that the substance is not pure, and qualitative tests for sulphur and nitrogen show the presence of both. This indicates that the fusion with potassium hydroxide was not complete. Therefore, what remained of the substance was again fused with potassium hydroxide. This time the temperature was raised somewhat higher than before, and the fusion continued for about ten minutes. The mass, on cooling, became yellowish brown. This was dissolved in water, evaporated and extracted with ether. The residue consisted of a crystalline crust on the beaker, which was studded with fine white needles. The former melted at about 130° and the latter at 155°. Both portions were carefully tested with phthalic anhydride for resorcin, but no trace of fluoresceïn was formed. With ferric chloride the color was exactly that given by salicylic acid, and not that given by resorcin. In order to separate the acid from the dihydroxybenzene, in case they should both be present, the substance was treated with a solution of sodium carbonate, and then extracted with ether, which would take the dihydroxy derivative and leave the sodium salt of the acid in the water. The ether extract was evaporated, leaving a small impure residue which melts through a range of 15°, from 120°–135°. The ferric chloride color reaction was exactly that of salicylic acid. It is difficult to account for any salicylic acid here.

The small amount of material and the lack of time makes a further study of this question impossible at this time, and it is with regret that the author is obliged to leave for the present the question unanswered as to the position of the sulphonic acid group in the compounds above described.

Oxidation of Orthomethoxytoluene.

In order to furnish additional evidence that the formula of the oil obtained by the decomposition of orthodiazotoluene sulphate by methyl alcohol is $C_6H_4 \begin{matrix} CH_3 & (1) \\ OCH_3 & (2) \end{matrix}$, some of the oil was oxidized as follows:

Thirteen grams of potassium permanganate were dissolved in about 700 cc. of water in a flask fitted with a return condenser, and 5 grams of the oil were added. The mixture was heated on the water-bath, with frequent shaking, for about three hours, when the reduction of the permanganate was complete. The oxides of manganese were filtered off and the clear solution evaporated to about 100 cc. This was then acidified with hydrochloric acid. Upon cooling, beautiful fern-like crystals separate. After recrystallization these melt at 98.5°–99°, thus agreeing closely with orthomethoxybenzoic acid, which is described by Cahours[1] as melting at 98°.

Conclusions.

The foregoing investigations show:

1. That the orthodiazotoluene sulphate is decomposed by methyl alcohol at a lower temperature than the corresponding para compound.

2. That orthodiazotoluene sulphate, when decomposed by methyl alcohol under atmospheric pressure, gives almost exclusively the alkoxy reaction.

3. That whether the decomposition takes place slowly at the temperature of the room, or rapidly at a temperature near the boiling-point of the alcohol, makes practically no difference in the yield of the methoxy product.

4. That when orthomethoxytoluene is poured into cold concentrated sulphuric acid only one sulphonic acid is formed.

5. That the sulphonic acid so formed is a monobasic acid containing only one sulphuric acid residue.

6. That by oxidation, orthomethoxytoluene yields orthomethoxybenzoic acid.

1 Ann. chem. (Liebig), **42**, 60; *Ibid*, **92**, 315.

Biographical.

The author of this dissertation, William Bromwell, was born near Port Deposit, Maryland, February 24, 1866. His preparatory course of study was carried on at West Nottingham Academy, Maryland, and in 1884 he entered the Johns Hopkins University, where he received the degree of Bachelor of Arts in 1888. Since then he has spent nearly three years as chemist to the Museum of Hygiene, Washington, D. C., and the rest of the time as a graduate student at this institution, studying chemistry, with mineralogy and geology as subordinate subjects.